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ASSESSMENT OF CURRENT ISO PHYSICAL AND METALLURGICAL METHODS FOR DETERMINING THE QUALITY OF IRON ORE MATERIALS

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ASSESSMENT OF CURRENT ISO PHYSICAL AND METALLURGICAL METHODS FOR DETERMINING THE QUALITY OF IRON ORE MATERIALS

by

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ABSTRACT

This report to the Canadian Advisory Committee of ISO Technical Committee 102-Sub-Committee 3, concerned with the physical and metallurgical testing of iron ore materials, describes CANMET investigations of the free-swelling, and reduction disintegration testing of iron-ore materials. Permissible variability of gas flow rates appears satisfactory for the reduction disintegration of most high quality pellets but further investigation is required for sinters, and iron ores. The measurement precision for the free-swelling of iron oxide pellets appears to depend on the quality variation within the test sample. Results contributed by other member countries to the five active Working Groups of SC 3 are also summarized. The status of SC 3 documents recently reviewed is included.

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INTRODUCTION

Large modern blast furnaces producing upwards of 10,000 tonnes per day of pig iron require burden materials with chemical, metallurgical and physical properties that will ensure high productivity. Both coke and iron-ore materials must meet increasingly stringent specifications to improve blast furnace productivities and to decrease coke rates.

For evaluating the quality of iron ores, pellets, and sinters, it is no longer sufficient to analyze just for chemical and physical properties. It is becoming increasingly important to evaluate these materials, also, under metallurgical conditions simulating those in the blast furnace. It is accepted that poor reducibility, excessive swelling, early softening and high disintegration of iron ore materials have negative effects on blast furnace operation.

Currently, standard test procedures to evaluate iron-oxide materials under simulated blast furnace conditions are being developed within the forum of the International Organization for Standardization (ISO)*. In Canada, facilities to develop such test procedures have been established at CANMET, Ottawa. Investigations are planned in conjunction with the Canadian Advisory Committee (CAC) to ISO Technical Committee 102 Sub-Committee(SC)-3 with members from the major Canadian iron ore and steel companies. When standardized, specifications from these tests will be included into contracts for the buying and selling of iron oxide sinters, lump ores and pellets. Current contracts generally require only chemical and size analyses, and compressive and tumbler strengths to assess iron ore quality.

CURRENT PROGRAM OF SUB-COMMITTEE 3 (TC 102)

Proposed procedures for tests developed by SC3 are listed in Table 1. Such procedures, however, have a history of being constantly revised. To hasten the development of test proposals to the status of draft international standards (DIS) it was decided at the 1978 international meeting of SC-3 held in Australia that five new working groups (WG) would be established. Each WG would investigate

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*The Member Body for Canada is the Standards Council of Canada (SCC). The Canadian National Committee on ISO(CNC/ISO), acting on behalf of the SCC in work relating to ISO, has Canadian advisory committees reporting to it which provide the necessary expertise and representation of Canadian interests related to specific technical committees.

TABLE 1. Details of Test Procedures for Assessing Iron Ore Quality

Test	Equipment	Sample	Temperature	Composition of Reducing Gas	Reduction time	Results Reported
Reducibility	Loss-in wt. method; stainless-steel retort-75 mm I.D. suspended from balance	500 g -12.5 + 10.0 mm	950 ± 10° C	40:60, CO:N_2 50 l/min, STP	To 65 per cent O_2 loss or 4 h.	Rate of O_2 loss (dR/dt %/min) at 40 per cent reduction
Relative Reducibility	as above	as above	900 ± 10° C	30:70, CO:N_2 15 l/min	3 h.	% reduction after 3 h.
Low Temperature Disintegration	as above, tumble cold 10 min at 30 rpm in 200x130mm tumbler drum	as above	500 ± 10 °C	20:20:60, CO:CO_2:N_2 20 l/min, STP	1 h.	% of material after tumbling greater than 6.3 mm, 3.15mm & 0.5mm
Free-swelling	as above, with 18 pellets suspended individually in retort	18 pellets -12.5 + 10.0 mm	900 ± 10 °C	30:70, CO:N_2 15 l/min STP	1 h.	Percentage increase in volume measured by Hg displacement
Reduction-Under-Load	stainless-steel retort, suspended from balance, with 0.5 kg/cm^2 load applied	1200 g -12.5 + 10.0 mm	1050 ± 5 °C	40:60, CO:N_2 83.3 l/min STP	To 80 per cent O_2 loss	Change in differential gas pressure & shrinkage across sample bed to 80% Oxygen loss
Tumbler Test	tumbler- 500mmx 1000 mm I.D., 2 lifters, 25 rpm 200 revolutions	15 kg.	ambient	-	-	per cent of sample after tumbling retained on 6.3 and 0.5 mm seives
Decrepitation of Ore	furnace capable of heating iron ore to 700 °C in 30 min.	500 g -25.0+20.0 mm	700 ± 10 °C	air	-	Per cent of product less than 5 mm after heating
Crushing test	loading unit with 1000 kg capacity applied at 15 mm/min	60 or more pellets, -12.5 + 10.0 mm	ambient	-	-	mean strength (kg)

one test method. Test procedures give priority are:

- Reduction Disintegration Test-DP4696, WG-2
- Relative Free Swelling Test-DP4698, WG-3
- Crushing Strength Test-DP4700, WG-4
- Reduction-Under-Load-SC-3 doc. 430, WG-5
- Relative Reducibility Test-SC-3 doc. 464, WG6

The CAC is a member of WG's -2, 3, and 5 of SC3 and has agreed to make available Canadian results of relevance to other WG's.

Reduction Disintegration Test (WG-2)

In the blast furnace, the reduction of iron ore to iron takes place through intermediate stages of magnetite and wustite. The reduction disintegration test measures the degradation of iron ore materials during the transformation of hematite to magnetite. Parameters for the static reduction disintegration test are listed in Table 1. This WG has been the most active of all in SC-3; Canada is an active member and has contributed to the following studies.

Flow Rate of Reducing Gas The sixth draft DP4696 proposes a total gas flow rate of 20 ± 1 1/min. CANMET has examined the effects of small changes in gas flow rate upon the reduction distegration indices (RDI) of acid iron oxide pellets used in Canada. Results of tests using flow rates of 18, 20, and 22 1/min are included in Table 2 (1). The present acceptable variability of gas flow appears satisfactory for high quality pellets B and C since changes in degradation indices were not significant for flow rate changes of $\pm$ 2 1/min. Even for pellet A, the larger changes in gas flow rate did not cause significant changes in RDI. However, because of the low reduction disintegration of most pellets, it is advisable that additional testing be carried out on sinters, ores, and pellets of poorer quality to confirm that variations of gas flow rates have no significant effects on test results.

Reducing Gas Variability Maximum allowable impurities in this test are 0.1% H_2, 0.1% O_2, and 0.2% H_2O. Sinters and hematite lump ores were tested at H_2 concentrations between 0 and 4%. Hydrogen concentrations up to 1% had no significant effect on reduction disintegration of lump ores and higher levels of 3.7 and 4.0% gave only marginal increases in breakdown. However, the results for all sinters

TABLE 2. Low Temperature Disintegration of Pellets as a Function of Reducing Gas Flow Rate

(Other conditions as specified in ISO/DP4696)

PELLET A

Gas Flow Rate litre/min	+6.35mm %	+3.35mm %	-0.5mm %
10	93.5	94.6	4.9
"	95.5	96.0	3.8
20	93.6	95.0	4.3
"	94.6	96.0	3.2
"	94.8	95.8	3.8
30	93.5	94.7	4.6
"	93.8	94.5	5.2

PELLET B

	18L/Min		20L/Min		22L/Min	
RDI + 6.30 mm	97.13	95.88	97.41	97.80	95.91	96.62
RDI + 3.15 mm	97.92	97.50	97.90	98.17	97.12	97.43
RDI - 0.5 mm	2.03	2.16	2.03	1.73	2.44	2.37
% wt loss	2.87	2.18	2.86	3.44	2.35	2.97

PELLET C

RDI + 6.30 mm	99.05	98.37	99.02	98.09	98.75	98.08
RDI + 3.15 mm	99.19	98.75	99.10	98.90	98.94	99.18
RDI - 0.5 mm	0.78	1.14	0.82	0.97	1.02	0.77
% wt loss	2.18	2.32	2.34	2.24	2.39	2.26

PELLET D

RDI + 6.30 mm	71.71	71.31	62.71	65.53	66.69	72.74	69.93
RDI + 3.15 mm	96.73	96.63	95.54	96.90	96.76	97.16	96.33
RDI - 0.5 mm	1.55	1.57	1.82	1.57	1.64	1.53	1.70
% wt loss	3.02	3.00	3.09	2.87	3.04	3.01	2.98

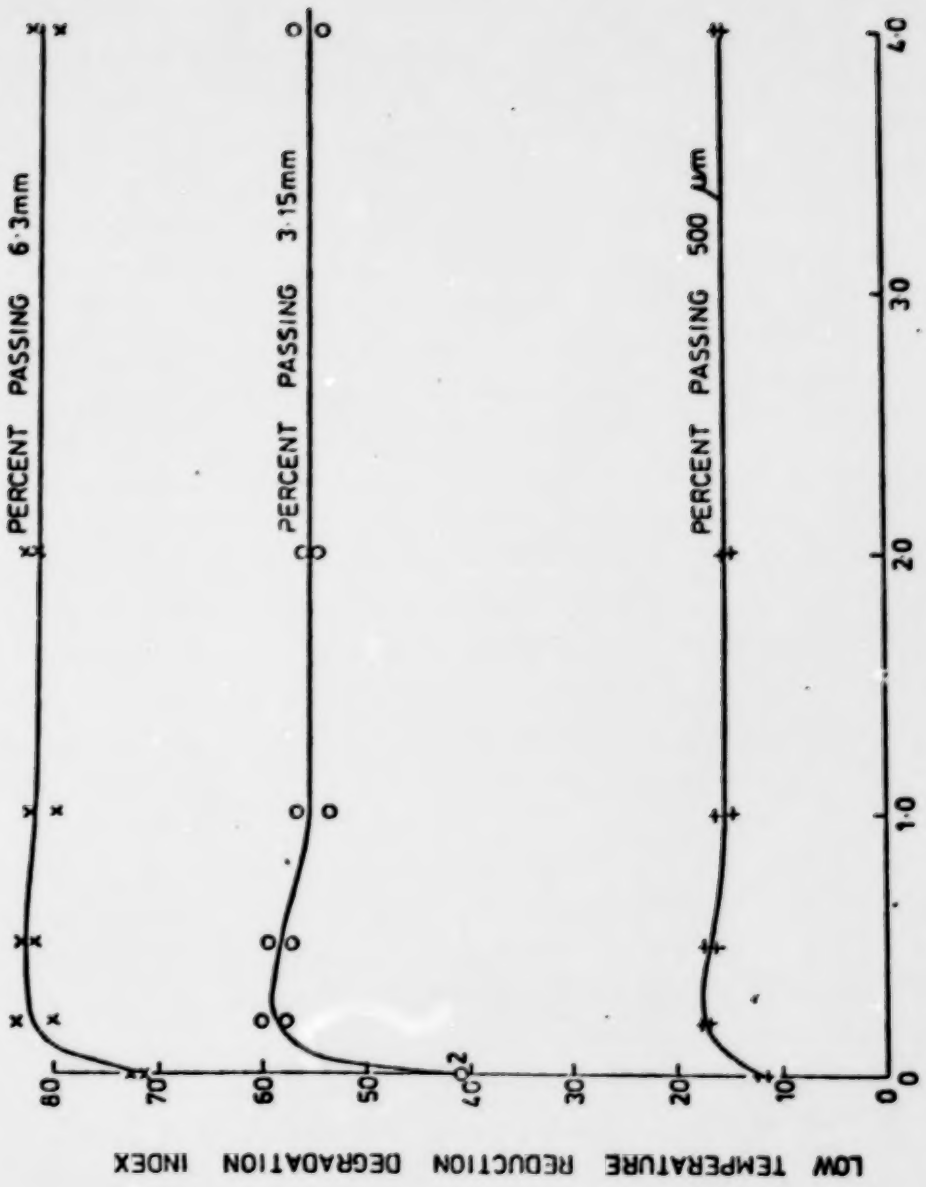

Figure 1. Low Temperature Reduction Degradation Index versus Hydrogen Addition. (Fluxed Sinter Sample A)

tested showed small percentages of H_2 caused a significant increase in degradation. Hydrogen concentrations greater than 1% had little further effect upon the disintegration indices. A typical result of sinter disintegration during reduction as a function of H_2 concentration is shown in Fig. 1.

Test Temperature The proposed temperature for this test is 500 °C. Results for two sinters tested at temperatures between 400 and 600 °C indicated maximum disintegration at about 500 °C (1) and temperature changes of ±10 °C, the current permissible variation, caused significant differences in degradation. A sample of pellets tested showed only marginal changes in degradation with test temperature. However, a CAC member laboratory investigating self-fluxed pellets found only small weight losses and disintegration after reduction at 500 °C. Using gas concentrations of 24% CO, 16% CO_2, 2% H_2 and 58% N_2 maximum degradation occurred at 400 °C but maximum reduction at 550 °C (2). Further investigation is warranted.

Preparation of Test Sample Draft proposal 4696 proposes sinters and ores be prepared by removing -10 mm material and carefully crushing of +12.5 material to just pass a 12.5 mm sieve. Tests have been completed to compare reduction disintegration results of ores and sinters prepared by three different methods: naturally sized 10.0-12.5 mm material: severely crushed material (all material passed through crusher to obtain size fraction); and carefully crushed material as proposed in DP 4696. There was no significant effect of sample preparation on the test results for sinters; naturally sized ores, however, gave unacceptable results (1).

Test Precision The CAC supplied data on precision of sampling and test measurement to SC-3 at the Australia meeting (3). Results were obtained by making duplicate measurements on two samples from each of 10 cargoes of pellets. The standard deviations of measurement were 1.8% for the 6.3 mm index; 1.48% for the 3.36 mm index and 1.46 for the 500 μm index. The chairman of WG-2 has asked all member countries to provide data from eight test measurements made on the same physical sample of material so that overall precisions can be established for ores, sinters, and pellets.

Relative Free-Swelling of Iron Oxide Pellets, WG-3

This test measures the swelling of iron oxide pellets under isothermal reductive conditions detailed in Table 1. Maximum swelling normally occurs at

30 to 40% reduction with swellings of up to 20% caused by volume changes during crystallographic transformation. This test will reveal catastrophic or abnormal swelling characteristics caused by iron whisker growth in the wustite-iron reduction step. Previous work has shown results are sensitive to pellet basicity, impurity levels, test temperature and reduction time (4,5,6). To determine test precision for WG-3, CANMET, has completed as many as eight relative free-swelling measurements using the new test conditions (Table 1) for each of three fluxed iron ore pellets and one acid pellet. Results are listed in Tables 3 and 4. Mean reductions for the four pellets tested had a range from 46% for the higher basicity (CaO/SiO_2) pellets to 63% for the acid pellet. For the same pellet type there were considerable differences in the amounts of reduction with standard deviations ranging from 1.6 to 3.4%. Pellets were reduced in the retort in two layers of nine pellets each. The bottom layer of pellets which encounters the reducing gas first was generally reduced more (3-9%) than pellets in the top layer. The acid pellet showed the highest reducibility and gave significantly different reduction levels for the top and bottom layers (t test 95% confidence level).

All pellets exhibited normal swellings with means from 2.7 to 18%. Standard deviations on significant tests for the free swelling index varied from 0.9 to 3.8% suggesting large quality variations of the different pellet types. The different amounts of reduction of the top and bottom layers for the acid pellet also caused significant swelling differences between the layers for this pellet. Because maximum pellet swelling normally occurs between 30 and 40% reduction, large differences in the amount of reduction after one hour could alter the relative magnitudes of the free-swellings for different types of iron ore pellets. Possibly continuous weight loss should be measured during reduction and the free swellings measured after reduction has reached, for example, 45%.

Using the new test conditions, fewer practical problems were encountered in measuring pellet volumes than had been found previously. In earlier testing using other pellet types, higher test temperatures, and higher partial pressures of CO; the mercury used to measure volume had penetrated the interiors of the swelled pellets giving false measurements.

Further international investigations have been proposed by the Swedish

TABLE 3. Per Cent Reduction for Free-Swelling Tests

Pellet Type	Per Cent Reduction								Stats. Results*	
(CaO/SiO_2)	1	2	3	4	5	6	7	8	$\bar{x}$	σ
Acid pellet										
top layer	58.3	52.7	65.6	57.0	56.5	61.1	60.1	56.6		
bottom layer	68.6	63.8	71.0	61.2	63.7	70.2	69.3	69.3		
total	63.2	58.2	68.2	59.9	60.2	65.6	64.8	64.8	62.8	3.4
CaO/SiO_2 0.67										
top layer	57.0	51.0	50.0	50.7	48.5	51.9	55.5	59.3		
bottom layer	59.0	54.1	58.7	50.4	62.0	54.3	53.1	60.1		
total	57.9*	52.5	54.1	50.6	55.0	53.1	54.3	59.6	54.2	2.81
CaO/SiO_2 1.17										
top layer	41.9	46.3	43.7	38.5	24.9	44.6	46.5	40.4		
bottom layer	53.3	50.9	49.8	46.8	39.2*	50.1	51.6	46.5		
total	47.8	48.6	46.8	42.5	32.4*	46.5	49.1	43.4	46.4	2.53
CaO/SiO_2 1.20										
top layer	48.1	46.0	44.7	47.4	45.1	50.5	55.9	49.2		
botton layer	52.7	57.4	42.0*	54.2	48.5	49.4	46.8	51.0		
total	48.9	51.5	43.3	50.5	46.8	49.9	51.4	50.1	49.9	1.63

*Test result with a statistical outlier not used to determine $\bar{x}$ or σ

TABLE 4. Precision of Free-Swelling Measurements

Pellet Type	Per Cent Swelling								Stats. Results*	
(CaO/SiO_2)	1	2	3	4	5	6	7	8	$\bar{x}$	σ
Acid Pellet										
top layer	3.6	8.6	-1.3	5.4	6.0	0.6	8.2	3.4		
botton layer	-1.3	3.5	0.0	0.0	3.5	0.2	3.6	-2.2		
total	1.25	6.1	-0.7	2.7	4.8	0.4	5.8	0.6	2.6	2.64
CaO/SiO_2 0.67										
top layer	38.5	22.5	16.0	14.7	11.4	14.7	18.1	21.4		
bottom layer	31.5	25.3	23.2	12.0	17.1	15.8	15.7	20.0		
total	35.1*	24.0	19.4	13.3	14.3	15.2	16.9	20.7	17.7	3.86
CaO/SiO_2 1.17										
top layer	15.5	13.2	13.4	10.8	12.0	11.9	12.3	11.1		
bottom layer	7.2	13.3	8.4	10.0	13.2	12.2	10.5	12.0		
total	11.0	13.2	10.9	10.4	12.6*	12.0	11.4	11.5	11.5	0.92
CaO/SiO_2 1.20										
top layer	13.3	14.3	12.6	18.9	7.1	12.4	13.6	12.5		
bottom layer	9.5	22.1	10.9	10.0	9.6	8.7	11.8	11.4		
total	11.5	18.1	11.7	14.7	8.4	10.5	12.7	12.0	11.6	1.94

*Test result with a statistical outlier not used to determine $\bar{x}$ or σ

chairman of WG-3 involving round robin testing of three or four samples having different swellings at three temperatures (900-1000 ^{o}C), two gas compositions (30/70 and 40/60, CO/CO_2) and three gas flow rates (10, 15, and 20 l/min).

Crushing Strength of Iron Ore Pellets -DP 4700, WG-4

Working group 4 was formed primarily to determine the precision of this test method. The quantity of sample to be tested for crushing strength depends on the variability of the pellets and the precision desired. At present, the ISO proposed standard for this test requires a sample of at least 60 pellets of size -10.0 + 12.5 mm; precision of the test will be determined by the parties concerned. Although Canada is not a WG member, the CAC members agreed to forward precision results for pellet types tested in their laboratories to the chairman of WG-4. Companies providing results include DOFASCO, STELCO, INCO, and IOC. Two samples were tested (minimum of 30 pellets/sample) on several cargoes sampled by IOC in order to compare measurement and sampling errors. Results from other companies involved testing 50 or more pellets from one sample from each batch or cargo of pellets examined. The mean strength, standard deviations, and number of pellets tested for each pellet type are summarized in Table 5; detailed analyses are reported elsewhere (7,8). It was concluded from these reports that: results approximate normal distribution; the major error component is in the test measurement, not sampling; the number of pellets tested is the controlling factor for test precision.

TABLE 5. Crushing Strengths of Iron Oxide Pellets

Pellet type	Overall mean Strength-kg	Pooled σ	no. of pellets	Comments
A	228	89	4200	42 batches of pellets, 2 samples/batch
B	210	67	1188	20 batches of pellets, " " "
C	238	91	1100	22 batches of pellets, 1 sample/batch
D	510	134	60	1 batch of pellets, 1 sample/batch
E	491	138	60	" " " "
F	229	81	60	" " " "
G	492	150	60	" " " "
H	250	114	400	8 batches of pellets, "

Reduction-Under-Load Test, WG-5

Since the last SC-3 meeting in Australia, no work has been done in Canada on this test procedure, which measures the differential gas pressure and shrinkage of a bed of iron ore material during reduction. Test conditions are given in Table 1. Canada is a member of WG-5 although it has not supported this test becoming an ISO standard because of precision difficulties found in previous investigations (9). Similar difficulties encountered in recent round-robin testing in Germany have been supposedly overcome. Germany has therefore submitted three pellet types for round robin testing to laboratories of seven WG members with special instructions concerning difficulties associated with test execution. CANMET will participate in this round-robin work.

Relative Reducibility Test for Iron Ore Materials, WG-6

The relative reducibility test measures the relative rates at which iron ore can be transformed to sponge iron, simulating gas-solid reactions occuring in the stack of the blast furnace. This test procedure was introduced at the Australia meeting of SC-3 as an alternative to the reducibility test which requires high flows of costly CO reducing gas. This procedure is a modification of the Japanese standard (10) and reduces gas flow rates to 15 l/min. In Canada, one CAC member has indicated little saving at flows of 20 versus 50 l/min because of added labour costs associated with increased test time to reach the same degree of reduction.

Sub-Committee-3 formed WG-6 in Australia to investigate the precision of the method when testing lump ores. The CAC did not participate because Canada does not market lump ore. Test results on nine ores from five countries are summarized in Table 6. Each type of ore was divided and reduced into 4 samples with duplicate tests made on each sample. Results show permissible tolerances vary from 2.1 to 23.3% depending, probably, on the inherent mineralogical properties of the natural ores. It was concluded that permissible tolerances for natural ores should not be specified in an International Standard.

The proposed standard permits tolerances between two individual results of 3% for pellets and 5% for sinter. No data, however, has been provided to SC3 to support these values.

TABLE 6. Precision Results for Relative Reducibility of Lump Ores

Sample	$\bar{x}$	$\bar{R}$	σ	$D_2\sigma$ (In per cent)
Ore A	54.05	3.45	2.86	10.53
Ore B	53.48	1.78	1.47	5.42
Ore C	40.05	3.05	2.52	9.31
Ore D	51.64	2.23	1.84	6.79
Ore E	53.74	6.38	5.28	19.46
Ore F	38.94	2.36	1.96	7.21
Ore G	35.93	0.70	0.58	2.14
Ore H	40.79	2.63	2.17	8.01
Ore I	62.50	7.65	6.33	23.33

x_1 - test result, $\bar{x}$ - mean reducibility of 4 samples tested in duplicate, $\bar{R}$ - $|x_1 - x_2|$ for duplicate tests, $D_2\sigma$ - permissible tolerance (3 sigma-basis) $\sigma = \bar{R}/1.208$

DOCUMENTS UNDER REVIEW

Table 7 summarizes the status of documents reviewed by CAC members of SC3 since the September 1979 meeting held at SCC, Mississauga Ont.

TABLE 7. SC-3 Documents Under Review By the CAC

Doc. No.	Deadline	Subject	Comments
N 459 (JA-71)	1980-01-15	Decrepitation index	Not Approved
N 461 (AU-26)	1980-01-15	Decrepitation index	Not Approved
N 460 (WG6-2)	1980-01-15	Rel. Fed. results	Approved with Comments
N 464 (WG6-3)	1980-03-21	Rel. Red. test proposal	Disapproved with reasons
ISO 3271	1980-04-30	Tumbler test - review	Approved with Comments
Agenda	1980-05-23	SC3 Meeting, S. Africa	To be voted on

REFERENCES

1. ISO/TC 102/SC3-WG-2; "Review of Test Programme Results", Central Research Laboratories Report, BHP, Australia, March 1980.

2. Minutes of the Special Meeting of CAC ISO TC 102/SC 3, Mississauga, Ontario, Sept. 1979.

3. "A Need to Determine Specifications for Permissible Tolerances of Results from Reducibility, Tumbler, and LTD Test Method", ISO/TC 102/SC 3 (CA-26) 421E, Nov. 1978.

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6. Price, J.T., and Reeve, D.A., "The Free-Swelling Behaviour of Iron Oxide Pellets"; Energy Research Laboratories Report MRP/ERP 75-146(TR), CANMET, 1975.

7. Sutarno, R., and Bowman, W.S., "Precision of Test for Crushing Strength of Iron Ore Pellets"; Mineral Sciences Laboratories Report MRP/MSL 79-128(IR), CANMET, 1979.

8. Sutarno, R., private communication.

9. Price, J.T., and Reeve, D.A., "Comparison of the Burghardt and Hoogovens Methods for Measuring the Softening-Under-Load Characteristics of Iron Oxide Pelelts"; Energy Research Laboratories Report MRP/ERL 75-78(IR), CANMET, 1975; ISO/TC 102/SC 3 (CA-13) 313, 1975.

10. Japanese Industrial Standard; JIS M8713-1972.

11. ISO/TC 102/SC 3 (WG6-2) 460; 1979.